Heat of Crystallisation of Quartz.

By Rames Chandra Ray, M.Sc.

(Communicated by Dr. M. W. Travers, F.R.S. Received April 26, 1922.)

1. *Introductory.*

Several attempts have been made to determine the heat of crystallisation of quartz, or the heat of transformation of quartz into vitreous silica, which is of importance in calculating the heat change involved in silicate reactions, and conflicting results have been obtained by different workers. Tschernobaeff[*] determined the heats of formation of certain silicates by Le Chatelier's method,[†] measuring the heat evolved when a mixture of the dry substances were made to react by combustion of a given weight of carbon in a bomb calorimeter. From the difference of heat of reaction of silica glass and calcium carbonate, and of that of sand and calcium carbonate, Tschernobaeff found that the heat of transformation of quartz into vitreous silica was very small, and equal to only 0·9 Kgrm.-cals. per grm.-molecule. But from the results published later by Tschernobaeff and Wologdine[‡] Dr. M. W. Travers has calculated the heat of transformation of silica and found it to be equal to 7·3 Kgrm.-cals.[§]

From the measurements of conductivity, Tammann[||] showed that amorphous and crystalline silica dissolved in hydrofluoric acid in one and the same state, so that the difference between the heats of solution of the two substances would represent the heat of transformation from the crystalline to the vitreous state. Cunningham[¶] was the first to use the hydrofluoric acid method for this purpose. His experiments, however, were more or less of a qualitative nature, but he stated that he obtained a distinct indication of a large difference between the heats of solution of crystalline and vitreous silica.

The difficulty of determination by this method lies in the fact that the reaction, especially in the case of quartz, is extremely slow. The same method was employed later by Mulert[**] and Wietzel[††] in order to determine the heat of crystallisation of silica. Both of them obtained very nearly the same value for the difference between the molecular heats of solution of crystalline and vitreous silica, namely, 2·21 and 2·32 Kgrm.-cals. respectively. But it will be shown in this paper that these values are far too low and that the error is probably due to the fact that, in order to obviate the slowness of the reaction, both these workers subjected their samples to long grinding, which causes a considerable increase in the heat of solution in the case of the crystalline material. In the case of Mulert's experiments, the quartz was ground in an agate mortar for 17 hours, and then the powder was subjected to a special washing process to separate the finest particles. Finally, he obtained about 1 grm. of substance from 1 kgrm. of the powdered quartz. Rock crystal, which was used in Wietzel's experiments, was ground in a mechanically operated agate mortar for 100 hours.

---

[*] 'Rev. de Métallurgie,' vol. 2, pp. 729–736 (1905).

[†] 'C. R.,' vol. 120, p. 623 (1895).

[‡] 'C. R.,' vol. 154, p. 208 (1912).

[§] 'Jour. Soc. Glass Tech.,' vol. 4, p. 220 (1920).

[||] 'Kristallisieren und Schmelzen.'

[¶] 'Proc. Roy. Dub. Soc.,' New Series, vol. 9, p. 412 (1901).

[**] 'Zeit. f. Anorg. Chem.,' vol. 75, p. 206 (1912).

[††] *Ibid.*, vol. 116, p. 75 (1921).

2. *Method of Determination. Analysis and Determination of Specific Heat of Aqueous Hydrofluoric Acid.*

Preliminary determinations of heats of solution were carried out with a thermometer coated with wax to prevent it from being attacked with hydrofluoric acid. These gave the necessary experience, and showed that the difference between the molecular heats of solution of quartz and silica glass was approximately equal to 7 calories. Silver sand was used for crystalline silica, and it was found that particles which passed through a 20-mesh sieve were quite suitable for the reaction. In the case of silica glass, however, particles which passed through a 40-mesh sieve had to be used; for, if finer particles were used, the reaction proceeded too rapidly to follow the rise of temperature easily. It was found that this difference in the size of the particles did not appreciably affect the heats of solution, for silica glass which was passed through a 20-mesh sieve gave almost the same heat of solution as that passed through a 40-mesh sieve.

The final determinations were carried out with a thermometer divided into tenths of a degree. The bulb of the thermometer was protected with a platinum cap which was especially constructed to fit the bulb of thermometer closely. A small quantity of mercury was introduced into the cap to obtain an intimate contact between it and the bulb of the thermometer. The top of the cap was attached to the stem of the thermometer with a small piece of rubber tubing. The calorimeter vessel was a platinum crucible of about 60 c.c. capacity, which fitted tightly into the bottom of a fairly long Dewar's vessel, the mouth of which was closed with cotton-wool during the experiment. The thermometer itself was used as the stirrer.

The silver sand used in the determinations was first freed from finer particles by sieving, and those particles which passed through a 20-mesh sieve were purified by boiling repeatedly with hydrochloric acid, then washing with distilled water and drying at 150° C. The silica glass, obtained from the British Thermal Syndicate, was broken into small pieces by a hammer, and then crushed in an agate mortar. The particles which passed through a 40-mesh sieve were boiled with hydrochloric acid, washed, and dried in the same way as the sand.

The hydrofluoric acid used was found to possess approximately a specific gravity of 1·17 at the ordinary temperature. The acid was analysed in the following manner:—

A weighed quantity of the acid in a platinum dish was diluted with water, and an excess of sodium carbonate was added. A large quantity of ammonium carbonate was then added, and the solution was heated. After standing for 12 hours, the precipitated silicic acid was filtered. The filtrate was treated with a small quantity of ammoniacal zinc oxide solution, boiled until the ammonia was completely expelled, and the precipitate of zinc silicate and oxide was filtered and washed with water. The precipitate was treated with hydrochloric acid, and the silicate, obtained by evaporation on the water bath in the usual way, was added to the silica obtained in the first operation. The filtrate, after treatment of the ammoniacal zinc oxide, was treated with an excess of calcium chloride solution, filtered and washed with hot water. The precipitate was dried and ignited in a platinum crucible. After cooling it was carefully treated with an excess of acetic acid and evaporated to dryness on a water bath. The dried mass was taken up with water, filtered, washed free from calcium acetate, dried and ignited. The following results were obtained:—

No. of experiment.	Percentage of SiO_2.	Percentage of H.F.
I	0·89	34·59
II	0·86	34·64
Mean	0·88	34·62

The specific heat of the hydrofluoric acid was measured by a slight modification of the method described by Müller-Pfaundler.* The same current of electricity was passed through the same resistance of fine platinum-iridium wire for the same time into weighed quantities of the aqueous hydrofluoric acid and water placed in the same vessel. The initial temperature of the liquids was as much below the ordinary temperature as the final temperature was above it, so that the loss of heat during the experiment which lasted from 8 to 10 minutes, and the alteration of the resistance of the wire by temperature, were practically eliminated. If m be the weight of hydrofluoric acid, c its specific heat, t^0 the rise of temperature, and m^1 the weight of water, c^1 the specific heat of water, t^1 the rise of temperature, then $mc+w/m^1c^1+w = t^1/t$, where w is the water equivalent of the calorimeter. The following values were obtained for the specific heat of different strengths of hydrofluoric acid:—

---

* 'Lehrbuch der Physik,' 8th ed., vol. 2, p. 2311.

Table I.

Percentage of HF (by weight) in solution.	Specific heat.
10	0·908
20	0·838
30	0·756
34·6	0·724

3. *Determinations of the Heats of Solutions of Quartz and Silica Glass.*

In order to determine the heat of solution, a definite quantity of hydrofluoric acid (29·40 grm.) was introduced into the calorimeter, and stirred by means of the thermometer as already described, and the temperature noted at intervals of 1 minute. After 3 to 5 minutes a weighed quantity of the purified and dried silver sand, or silica glass, was quickly poured into the calorimeter and the rise of temperature was noted after every minute with constant stirring. The action was allowed to continue from 15 to 25 minutes, and was then stopped by adding a large quantity of cold water. The quantity of material used in different experiments varied between 3 and 8 grm. In the case of the silver sand, 0·3 to 0·6 grm. of the substance dissolved and the rise of temperature was never less than 6° C.; whilst in the case of the silica glass as much as 1·4 grm. of the substance dissolved and the rise of temperature was as high as 34° C. After the reaction had been stopped, the contents of the calorimeter was washed out, and the undissolved silver sand, or silica glass, as the case might be, was filtered off, washed with water, and weighed. From the loss of weight, the amount of silica dissolved could be determined. In two cases, the amount of silica in solution was estimated directly, and the amounts dissolved were found to be the same as those calculated from the weight of the undissolved silica, showing that no loss of silica took place, during the reaction, as silicon tetrafluoride.

Mulert (*loc. cit.*) has shown that when silica is treated with aqueous hydrofluoric acid only hydrofluorsilicic acid is formed, six molecules of the acid taking part in the reaction for each molecule of silicon dioxide. The loss of heat on account of radiation was determined separately for each experiment, by determining the rate of cooling of water with the same amount of sand or silica glass. Knowing the loss of heat in the case of water, the loss in the case of hydrofluoric acid could be calculated; for the quantities of heat given off in the same time would depend on the weights of the liquids and their specific heats. The following table gives the details of experiments and the results obtained:—

Table II.

Substance.	Size of particles.	Weight of substance added in grms.	Weight of substance dissolved in grms.	Time of reaction in mins.	Rise of temperature.	Water equivalent of calorimeter.	Heat of solution per grm.-mol. in Kgrm.-calories.
Silica glass ...	40-mesh	6·4090	1·1550	14	28·80	4·67	37·33
„ „ ...	„	6·7048	1·0744	13	25·32	4·67	37·04
„ „ ...	„	5·2174	1·3620	16	32·98	4·67	37·27
„ „ ...	„	3·3098	0·5566	11	13·29	4·67	37·36
„ „ ...	20-mesh	4·7622	1·4689	7	34·40	4·67	37·22
Silver sand ...	„	8·0914	0·6044	22·5	11·30	4·67	30·32
„ „ ...	„	7·7712	0·6016	25	11·23	4·67	30·18
„ „ ...	„	5·2337	0·3668	16	7·01	4·67	30·38
„ „ ...	„	4·0620	0·3127	13	6·02	4·67	30·29
„ „ ...	„	3·8746	0·4938	20	9·50	4·67	30·30

The mean of the values of the heats of solution of silica glass in hydrofluoric acid is 37·24 Kgrm.-cals. per grm.-molecule of silicon dioxide, and that for silver sand is 30·29 Kgrm.-cals. per grm.-molecule. The difference between the two heats of solution is 6·95 Kgrm.-cals. Therefore the heat of crystallisation of quartz at the air temperature may be represented thus:—

$$SiO_2 \text{ (vitreous)} = SiO_2 \text{ (quartz-cryst.)} + 6{\cdot}95 \text{ Kgrm.-cals.}$$

This value is of the same order of magnitude as that calculated from Tschernobaeff and Wologdine's results, and is much higher than those obtained by Mulert and Wietzel.

4. *Change in the Heat of Solution of Quartz and Silica Glass ground for a long time.*

In taking up this investigation, it was anticipated that the low value of the heat of transformation of silica obtained by Mulert and Wietzel (*loc. cit.*) would be found to be connected with the fact that they submitted the crystalline material to prolonged grinding. Sir George Beilby has shown that grinding of crystalline substances to powder does not simply consist in their reduction to finer and finer crystalline fragments, but it involves the transformation of, at any rate, a part of the substance into the vitreous condition.* Hence it was considered worth while to study the effect of long grinding on silver sand as well as silica glass.

The silver sand and silica glass which were used in the above experiments were separately ground, for 15 hours each, in a mechanically operated agate mortar. The powders thus obtained were very fine, and passed completely through a 200-mesh sieve. They were again dried at 150° C., and the heats of solution were determined in the usual way. As the finely powdered substances dissolved readily it was not necessary to add the material in excess as in the case of the experiments described above. In the following experiments the substance added was entirely dissolved. The following are the results of the experiments:—

Table III.

Substance (ground for 15 hours).	Amount added in grms.	Rise of temperature.	Water equivalent of calorimeter.	Time of reaction in mins.	Heat of solution per grm.-mol. in Kgrm.-calories.	Mean.
Silica glass	0·7004	16·01	4·67	7	36·93	36·95
" "	0·4786	11·50	4·67	5	36·96	
Silver sand	0·8080	17·09	4·67	12	32·47	32·46
" "	0·4526	9·62	4·67	9	32·45	

It will be noticed that grinding has a considerable influence on the heats of solution in the case of the quartz. The molecular heat of solution of silver sand which was ground for 15 hours was found to be 2·17 Kgrm.-cals. higher than the one which was not subjected to grinding. Using a 35-per-cent. hydrofluoric acid solution Wietzel (*loc. cit.*) found 33·65 cals. as the heat of solution of rock crystal which had been ground for 100 hours. It is evident that the action of grinding modifies the crystalline material, and partially converts it into the vitreous form. It s clear from the results of the experiment that the increased heat of solution of the ground substance is not due to the increased heat of hydration on account of the fineness of the particles. The slight lowering of the heat of solution of silica glass on grinding, however, is not easily explained. All the samples used for the experiments were very kindly examined by Mr. H. Mitter, M.Sc., who is working in Prof. Bragg's laboratory, by the X-ray method, and he could not find crystalline material in any of the samples of silica glass. This is in accordance with the results obtained by Kyropoulos,[*] who examined finely powdered silica glass.

---

* 'Aggregation and Flow of Solids,' p. 119 (1921).

5. *Heat of Crystallisation of Quartz at Higher Temperatures.*

The latent heat of crystallisation of quartz at higher temperatures can be calculated by means of the expression

$$(\mathrm{Ccr}-\mathrm{Cgl})\,t = \mathrm{Lo}-\mathrm{Lt},$$

where Ccr and Cgl are the mean interval molecular heats of the crystalline and glassy materials, and Lo and Lt are the molar latent heats at 0° and t° respectively. The values of Ccr and Cgl can be obtained from the mean interval specific heats, which have been determined by White[†] for intervals between 0° and temperatures up to 900° C. It was found that, contrary to the usual experience, the value of Cgl is less than that of Ccr over the range of temperature investigated, the difference between the values attaining a maximum at about 700°, then diminishing and having a tendency to coincide near the melting-point. The mean interval molecular heats in Kilogram-calories per gram-molecule at 900° are:—

Quartz	0·015576
Silica glass	0·015072

so that
$$(\mathrm{Ccr}-\mathrm{Cgl})\times 900 = 0{\cdot}45$$
and
$$\mathrm{L}900 = 6{\cdot}50.$$

At higher temperatures the difference would continue to diminish, and at 1300–1400° the value of Lt would probably not be far from the value at the air temperature. Finally, it may be mentioned that Washburn[‡] calculated the latent heat of fusion of crystobalite from the difference between the melting-point of crystobalite and the silica-alumina eutectic point and obtained the value 6·80 Kgrm.-cals. per molecule. This would also be approximately equal to the heat of crystallisation of quartz at the melting-point (1610°). Since the latent heat of the change,

$$\mathrm{SiO_2\,(quartz)} \rightleftarrows \mathrm{SiO_2\,(crystobalite)}$$

is probably very small, one would expect a close agreement between Washburn's value and that arrived at in the case of quartz.

---

[*] 'Zeit. f. Anorg. Chem.,' vol. 99, p. 198 (1917).

[†] 'Amer. J. Sci.,' vol. 47, p. 1 (1919).

[‡] 'Jour. Amer. Cer. Soc.,' vol. 2, p. 1008 (1919).

6. *Summary.*

(1) The specific heats of aqueous hydrofluoric acid of different concentrations have been determined and the results recorded in Table I.

(2) The heats of solution of quartz and silica glass in aqueous hydrofluoric acid have been determined (Table II), and the difference, which represents the heat of crystallisation of quartz at the ordinary temperature, is found to be equal to 6·95 Kgrm.-cals.

(3) From determinations of the heats of solution (Table III) it has been shown that grinding affects the crystalline material, which is partially converted into the vitreous state.

(4) The latent heat of crystallisation of quartz has been calculated at higher temperatures, and it is shown that near the melting-point the heat of crystallisation of quartz is very nearly equal to that at the air temperature.

My best thanks are due to Dr. M. W. Travers, F.R.S., at whose suggestion the work was undertaken, for the help I have received from him. I must also thank Prof. F. G. Donnan, F.R.S., for affording me the facilities in carrying out the work, and Mr. W. E. Garner, M.Sc., for the use of the platinum-iridium resistance.

The Properties and Molecular Structure of Thin Films.
Part III.—*Expanded Films.*

By N. K. Adam, M.A., University of Sheffield.

(Communicated by W. B. Hardy, Sec. R.S. Received May 4, 1922.)

1. *Expansion of Films of the Fatty Acids on Dilute HCl.*

In the previous paper an account was given of the properties of the films over a range of temperature low enough for it to be permissible to regard the molecules as in direct contact over the whole area, except perhaps for a very slight tendency to separate under the lowest compressions; this tendency being perhaps analogous to vapour pressure. The films in this condensed condition were either solid or liquid. Within the accuracy of my experiments, the mechanical properties of condensed films were independent of temperature.

The present paper describes the phenomena observed above this range of temperature. At a certain temperature all the films expand along the surface, the actual temperature of expansion depending both on the nature of the substance in the film, and on the composition of the solution. The phenomena exhibited by films of the fatty acids on dilute HCl have been the most thoroughly investigated, and will be first described.